Inorganica Chimica Acta, *177* (1990) 65–69

Ultraviolet and visible resonance Raman spectroscopy of tris-(2,2′-bipyridyl)iron(II): intensity considerations and band assignments

Robert M. Berger*
Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)
and **David R. McMillin**
Department of Chemistry, Purdue University, West Lafayette, IN 47907 (U.S.A.)

(Received July 14, 1989; revised June 4, 1990)

Abstract

Resonance Raman spectra of $Fe(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) have been recorded under excitation into two different metal-to-ligand $d \rightarrow \pi^*$ charge transfer absorption bands (λ_{ex} = 354.7 or 532.0 nm) of the complex. The relative intensities of the active intraligand vibrations exhibit a marked dependence on excitation wavelength. Normal modes assigned to distortions along the long axis of the bpy molecule are found to undergo greater relative enhancement under UV excitation, while those modes associated with large displacements within the diimine core are preferentially enhanced under visible excitation. These observations are consistent with the coefficients and the phase relations of the $2p\pi$ atomic orbitals of the lowest lying π^* orbitals of the bpy moiety as calculated by extended Huckel theory. Thus, the results lend strong support to previous assignments of the resonance Raman spectra of $M(bpy)_3^{2+}$ systems.

Introduction

Complexes of the type $M(bpy)_3^{2+}$, where M is in the iron group and bpy represents 2,2′-bipyridine, constitute a class of chromophore which has received considerable attention over the past two decades. The visible spectra are dominated by metal-to-ligand charge transfer (MLCT) transitions involving excitation into the lowest unoccupied π^* orbital of the bipyridine ligand. The next lowest energy orbital of bipyridine occurs about 1 eV to higher energy [1]. As discussed by Orgel [2] the two π^* orbitals are distinguished by their symmetry with respect to the mirror plane which bisects the bond between the 2 and 2′ carbons. The lower energy π^* orbital is symmetric with respect to the reflection (Fig. 1) and is designated as ψ. The higher energy, antisymmetric orbital is called χ. In $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ only the $d \rightarrow \pi^*$ (ψ) transition is well-resolved, but the MLCT transitions of $Fe(bpy)_3^{2+}$ are red shifted and both the $d \rightarrow \pi^*$ (ψ) and $d \rightarrow \pi^*$ (χ) transitions are resolved.

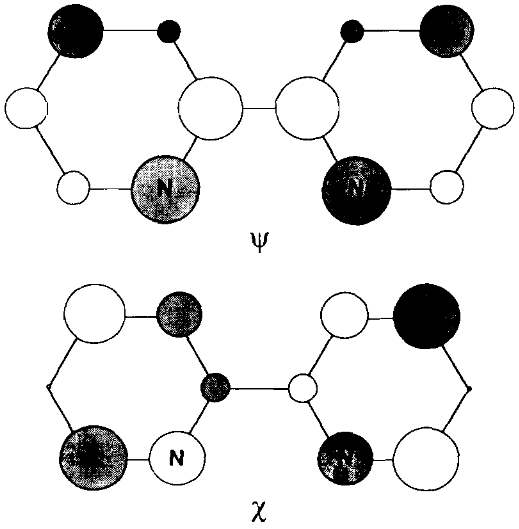

Fig. 1. Schematic representation of the relative magnitudes and signs of the coefficients of the $2p\pi$ atomic orbitals in ψ and χ, the two lowest unoccupied π^* molecular orbitals of 2,2′-bipyridine.

In the case of $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, the lowest energy MLCT excited states are reasonably long-lived (580 [3] and 19 [4] ns in aqueous solution

---

*Present address: Department of Chemistry, Indiana University–Purdue University at Fort Wayne, Fort Wayne, IN 46805, U.S.A.

0020-1693/90/$3.50

at room temperature, respectively) while that of $Fe(bpy)_3^{2+}$ has a much shorter lifetime (0.8 ns [4]). In addition to the electronic spectra, the resonance Raman and time-resolved resonance Raman spectroscopy of the $M(bpy)_3^{2+}$ systems have also been extensively investigated [5–15]. Resonance Raman scattering from the MLCT excited states of the Ru(II) and Os(II) complexes has been observed in a one pulse experiment using a frequency trebled Nd:YAG laser (*c.* 5 mJ per pulse) [7, 8], while at pulse energies up to 15 mJ per pulse, only scattering due to the ground state of $Fe(bpy)_3^{2+}$ can be observed.

Caswell and Spiro [16] have proposed assignments of the ground and excited state Raman spectra of $Ru(bpy)_3^{2+}$ by analogy with the biphenyl molecule whose normal modes of vibration have been studied in some detail [17]. In order to generate further support for the ground state assignments, we have measured the resonance Raman spectrum of $Fe(bpy)_3^{2+}$ by exciting into both the $d \rightarrow \pi^*$ (ψ) and the $d \rightarrow \pi^*$ (χ) absorption bands, and our results are discussed below.

Experimental

Materials

$[Fe(bpy)_3](ClO_4)_2$ was obtained from GFS Chemicals and used without further purification.

Instrumentation

UV–Vis spectra were obtained using either a Cary 219 or a Perkin-Elmer Lambda Array 3840 spectrophotometer. Resonance Raman spectra were recorded using a Nd:YAG laser based system previously described [18].

Methods

Solutions were prepared using doubly distilled/deionized water and were typically $5–10 \times 10^{-4}$ M in $Fe(bpy)_3^{2+}$. Na_2SO_4 was present at 1.0 M as an internal intensity/frequency standard. The spectra were collected using 90° excitation. The 354.7 nm spectrum was collected in the second order, while the 532.0 nm spectrum was collected in the first order. Band intensities in each spectrum were determined by the trace-and-weigh technique and corrected for reabsorption by a slight modification of the method of Spiro *et al.* [19].

A standard extended Huckel program was used to perform the MO calculations. The geometry of *cis*-2,2′-bipyridine was taken from Yagi *et al.* [20]. The relative magnitudes and signs of the coefficients of the $2p\pi$ atomic orbitals in the ψ and χ molecular orbitals are shown schematically in Fig. 1.

Results

The UV–Vis spectrum of $Fe(bpy)_3^{2+}$ is shown in Fig. 2. The band at 350 nm corresponds to a MLCT $d \rightarrow \pi^*$ (χ) transition [1] and has a molar extinction coefficient of 6600 M^{-1} cm^{-1}, while that at 520 nm corresponds to the $d \rightarrow \pi^*$ (ψ) MLCT transition [1] with an extinction coefficient of 8800 M^{-1} cm^{-1}.

The resonance Raman spectra obtained by excitation into each of these bands are presented in Fig. 3. The intense band at 982 cm^{-1} is due to the presence of SO_4^{2-}. The corrected intensities are given in Table 1. Each spectrum is dominated by bands which may be attributed to the skeletal vi-

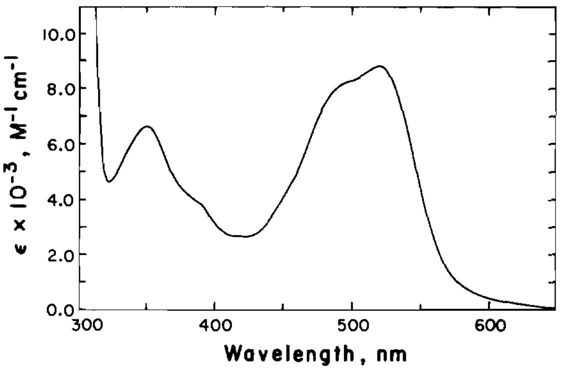

Fig. 2. Electronic absorption spectrum of $[Fe(bpy)_3](ClO_4)_2$ in aqueous solution. The MLCT $d \rightarrow \pi^*$ (ψ) and $d \rightarrow \pi^*$ (χ) transitions occur at 520 and 350 nm, respectively.

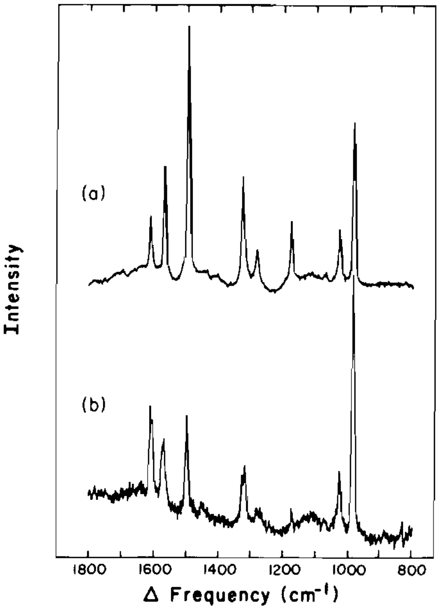

Fig. 3. Resonance Raman spectra of $Fe(bpy)_3^{2+}$ obtained by excitation at (a) 532.0; (b) 354.7 nm. The band at 982 cm^{-1} is due to the presence of 1 M SO_4^{2-} added as an internal frequency standard.

TABLE 1. Ground state resonance Raman frequencies and intensities for $Fe(bpy)_3^{2+}$ and correlations with biphenyl

Symmetry[a]	Mode[a]	Wavenumber (cm^{-1})	I_k (ψ)[b]	I_k (χ)[b]	Δ'_k (ψ)[c]	Δ'_k (χ)[c]	Δ'_k (ψ)/Δ'_k(χ)[c]
A_g	$\nu 4$	1608	0.27	0.79	0.48	0.70	0.69
B_{2u}	$\nu 3$	1566	0.59	0.57	0.72	0.61	1.18
A_g	$\nu 5$	1492	1.39	0.74	1.17	0.73	1.60
B_{2u}	$\nu 4$	1448	<0.01	0.10	<0.10	0.28	<0.36
A_g	$\nu 6$	1322	0.73	0.61	0.96	0.75	1.28
B_{2u}	$\nu 6$	1279	0.29	0.27	0.62	0.52	1.19
A_g	$\nu 7$	1174	0.41	0.19	0.80	0.47	1.70
B_{2u}	$\nu 8$	1068	0.07	0.13	0.37	0.44	0.84
A_g	$\nu 9$	1025	0.48	0.65	1.00	1.00	1.00

[a] Symmetry and modes of the biphenyl vibrations in D_{2h} symmetry, see refs. 16 and 17 and Fig. 4. [b] Corrected intensities of the resonance Raman bands under 532.0 (ψ) and 354.7 (χ) nm excitation, in arbitrary units. [c] See text for explanation of the symbols.

brations of the bipyridine ligands. While the Raman shifts are independent of excitation wavelength, the relative intensities of the bands exhibit a marked dependence on the excitation wavelength.

Discussion

The intensity changes observed in the Raman spectrum on passing from the non-resonance condition to the resonance condition reflect the changes in molecular geometry on passing from the ground state to the excited electronic state [21–25]. Because of its unique electron density distribution, the equilibrium structure of the excited state is distinct from that of the ground state. In the resonance Raman spectrum scattering is strongly enhanced for precisely those modes, normally totally symmetric vibrations, along which the displacement from the ground state structure occurs. The distinct intensity patterns observed in each of the resonance Raman spectra in Fig. 3 indicate that $Fe(bpy)_3^{2+}$ undergoes different distortions in the two charge transfer states.

Despite the fact that a wide body of data is available regarding the resonance Raman spectroscopy of the tris-bipyridyl complexes of Fe(II), Ru(II) and Os(II), assignments of the vibrational spectra of these complexes are rare in the literature. Recently, Kincaid and co-workers have published a normal coordinate analysis of $Ru(bpy)_3^{2+}$ [15]. Caswell and Spiro [16] have proposed assignments of the ground and excited state Raman spectra of $Ru(bpy)_3^{2+}$ with reference to the normal modes of biphenyl for which more detailed data are available [17]. In D_{2h} symmetry, the in-plane biphenyl modes are classified as A_g, B_{1g}, B_{2u} and B_{3u} if a standard coordinate system is imposed upon the biphenyl molecule with x along the long axis of the biphenyl molecule, y along the short axis, and z perpendicular to the plane of the molecule. If the same coordinate system is applied to the 2,2′-bipyridine molecule, the A_g and B_{2u} modes of biphenyl are found to correlate with the A_1 modes of 2,2′-bipyridine where y is a basis for A_1 in the C_{2v} subgroup. The same correlation is made by Caswell and Spiro [16], although there appears to be some confusion in their choice of axes. They base the assignment of the ground state resonance Raman spectrum of $Ru(bpy)_3^{2+}$ on frequency comparisons with the A_g and B_{2u} modes of biphenyl. Excellent correspondence is achieved with no modes being shifted by more than 50 cm^{-1}. The relevant normal modes of biphenyl are presented in Fig. 4 with the hydrogen atom contributions omitted for the sake of clarity.

In order to correlate the relative intensities of two bands in the Raman spectrum with their relative displacements, the following relationship can be used [26, 27].

$$\frac{I_k}{I_i} = \frac{\Delta_k^2 k^2}{\Delta_i^2 i^2} \tag{1}$$

In this equation I_k and I_i denote the intensities, at a given excitation wavelength, of the bands with frequencies k and i, while Δ_k and Δ_i denote the displacements of the corresponding modes. Strictly speaking, this equation is only applicable in the pre-resonance region or for excited states with extremely short lifetimes. In view of the sub-nanosecond lifetime of $Fe(bpy)_3^{2+}$, the errors are probably small. For each type of excitation ϕ, i.e. ψ or χ, we use the spectral intensities in conjunction with eqn. (1) to calculate $\Delta'_k(\phi)$ ($=\Delta_k/\Delta_{1025}$), the displacement along the normal coordinate with frequency k relative to that along the ring breathing coordinate which has been assigned to the band at 1025 cm^{-1} (Table 1). This choice of a reference coordinate is reasonable since all C–C and C–N bonds are affected roughly

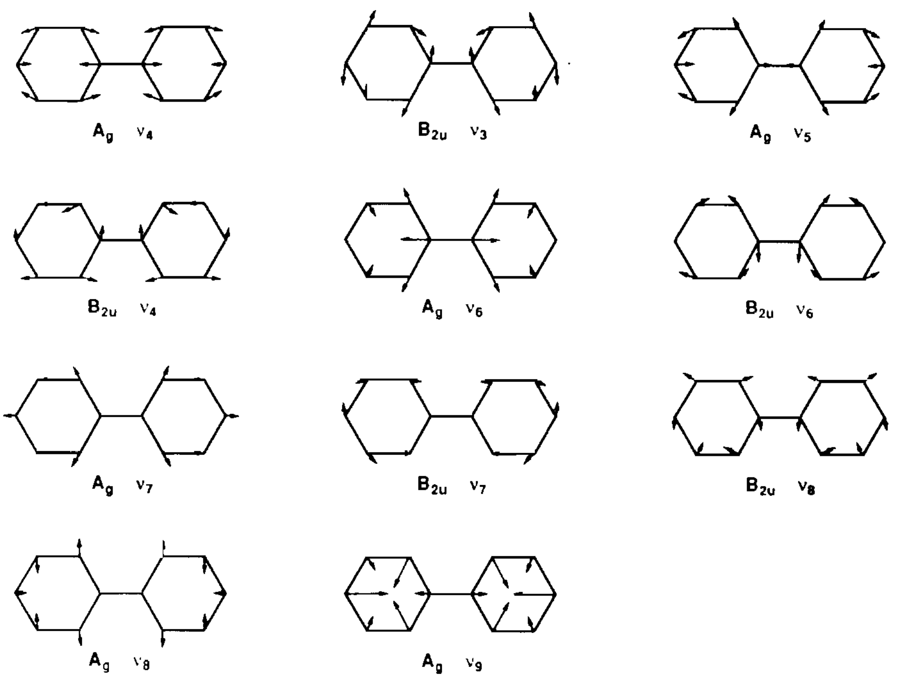

Fig. 4. Atomic displacements for the in-plane vibrations of the biphenyl molecule in D_{2h} symmetry, taken from ref. 17. The contributions of the hydrogen atoms have been omitted for the sake of clarity.

equally by the vibration; however, inferences drawn below would be evident regardless of which mode is used as the reference . Finally, $\Delta'_k(\psi)/\Delta'_k(\chi)$ is taken as an indication of the relative displacement that occurs in the excited state along a given normal coordinate for d → π^* (ψ) versus d → π^* (χ) excitation. The results in Table 1 suggest that the modes corresponding to the bands at 1566, 1492, 1322, 1279 and 1174 cm^{-1} experience a greater relative displacement with ψ excitation. Figure 4 reveals that in each case significant stretching of the C2–N, C2′–N′ and/or C2–C2′ bond is predicted to occur in the assigned normal mode of vibration. This is in accord with Fig. 1 which shows π^* (ψ) to be strongly antibonding between C2 and N and between C2′ and N′ and strongly bonding between C2 and C2′. On the other hand, according to the results in Table 1, the modes associated with the bands at 1608, 1068 and 1448 cm^{-1} experience a greater relative displacement with χ excitation. Fittingly, these bands are assigned to modes which involve significant deformation of the N–C6, N′–C6′, C3–C4 and C3′–C4′ bonds which are expected to undergo elongation upon population of π^* (χ); see Fig. 1.

Clearly, planar biphenyl and coordinated bipyridine are quite different chemical species in terms of structure and molecular symmetry. Nevertheless, qualitative intensity considerations are quite consistent with the proposal of Caswell and Spiro [16] that the skeletal vibrations of coordinated bipyridine can be correlated with normal modes previously assigned for the planar biphenyl molecule. Indeed, our results appear to be more consistent overall with the assignments of Caswell and Spiro than the more recent normal coordinate analysis by Kincaid and co-workers [28]. In particular, these authors assign the 1174 cm^{-1} band as essentially a CCH bending vibration. In view of the relatively strong enhancement with ψ excitation and the shift that this band undergoes on reduction of the ring system [29], the C_2–N stretching character seems likely to be important. It is also difficult to reconcile our results for the 1068 and 1608 cm^{-1} modes with the normal coordinate analysis where significant C_2–N and C_4–C_5 stretching, respectively, are assigned to these coordinates [28].

In conclusion, the resonance enhancements we observe with ψ and χ excitation are consistent with the proposed normal coordinates and a simple molecular orbital treatment. The agreement is surprisingly good in view of the fact that only two excitation wavelengths were available and different degrees of vibrational excitation within the electronic excited states are probably achieved. In addition, a referee has pointed out that the transition to the χ orbital is relatively weak and that pre-resonance effects from other states may also contribute to the observed intensity pattern for the short wavelength excitation.

Acknowledgements

The authors thank W. H. Woodruff and R. J. H. Clark for helpful discussions and suggestions and James Briggs for his valuable assistance in the molecular orbital calculations. This research was supported in part by NSF grant number CHE-8719538 (D.R.M.) and in part by the Office of Basic Energy Sciences of the Department of Energy (R.M.B.). This is Document No. NDRL-3213 from the Notre Dame Radiation Laboratory.

References

1 A. Ceulemans and L. G. Vanquickenborne, *J. Am. Chem. Soc., 103* (1981) 2238.

2 L. E. Orgel, *J. Chem. Soc.,* (1961) 3683.

3 J. Van Houten and R. J. Watts, *J. Am. Chem. Soc., 97* (1975) 3843.

4 C. Creutz, M. Chou, T. L. Netzel, M. Okumura and N. Sutin, *J. Am. Chem. Soc., 102* (1980) 1309.

5 R. J. H. Clark, P. C. Turtle, D. P. Strommen, B. Streusand, J. Kincaid and K. Nakamoto, *Inorg. Chem., 16* (1977) 84.

6 P. J. Miller and R. S. L. Chao, *J. Raman Spectrosc., 8* (1979) 17.

7 R. F. Dallinger and W. H. Woodruff, *J. Am. Chem. Soc., 101* (1979) 4391.

8 P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger and W. H. Woodruff, *J. Am. Chem. Soc., 103* (1981) 7441.

9 M. Forster and R. E. Hester, *Chem. Phys. Lett., 81* (1981) 42.

10 L. Griffiths, B. P. Straughan and D. J. Gardiner, *J. Chem. Soc., Dalton Trans.,* (1983) 305.

11 T. C. Strekas and S. K. Mandal, *J. Raman Spectrosc., 15* (1984) 109.

12 S. McClanahan and J. Kincaid, *J. Raman Spectrosc., 15* (1984) 173.

13 P. J. Carroll and L. E. Brus, *J. Am. Chem. Soc., 109* (1987) 7613.

14 C. V. Kumar, J. K. Barton, I. R. Gould, N. J. Turro and J. Van Houten, *Inorg. Chem., 27* (1988) 648.

15 P. K. Mallick, G. D. Danzer, D. P. Strommen, J. R. Kincaid, *J. Phys. Chem., 92* (1988) 5628.

16 D. S. Caswell and T. G. Spiro, *Inorg. Chem., 26* (1987) 18.

17 G. Zerbi and S. Sandroni, *Spectrochim. Acta, Part A, 24* (1968) 511.

18 S. F. McClanahan, R. F. Dallinger, F. J. Holler and J. R. Kincaid, *J. Am. Chem. Soc., 107* (1985) 4853.

19 T. C. Strekas, D. H. Adams, A. Packer, T. G. Spiro, *Appl. Spectrosc., 28* (1974) 324.

20 M. Yagi, K. Makiguchi, A. Ohnuki, K. Suzuki, J. Higuchi and S. Nagase, *Bull. Chem. Soc. Jpn., 58* (1985) 252.

21 C. H. Ting, *Spectrochim. Acta, Part A, 24* (1968) 117.

22 M. Tasumi, F. Inagaki and T. Miyazawa, *Chem. Phys. Lett., 22* (1973) 515.

23 A. Y. Hirakawa and M. Tsuboi, *Science, 188* (1975) 359.

24 M. Tsuboi and A. Y. Hirakawa, *J. Raman Spectrosc., 5* (1976) 75.

25 J. Tang and A. C. Albrecht, in H. R. Szymanski (ed.), *Raman Spectroscopy,* Vol. 2, Plenum, New York, 1970, Ch. 2, p. 33.

26 E. J. Heller, R. L. Sundberg and D. Tannor, *J. Phys. Chem., 86* (1982) 1822.

27 J. I. Zink, *Coord. Chem. Rev., 64* (1985) 93.

28 D. P. Strommen, P. K. Mallick, G. D. Danzer, R. S. Lumpkin, J. R. Kincaid, *J. Phys. Chem., 94* (1990) 1357.

29 J. B. Cooper, D. W. Wertz, *Inorg. Chem., 28* (1989) 3108.